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Poptube Technology, Enabling Multifunctional Hybrid Composites for Next Generation Aircrafts

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NASA Aeronautics Research Mission Directorate (ARMD)

LEARN Phase II Technical Seminar

September 6, 2017

Outline

- Background
- The innovation
- Mechanical Properties Characterization
- Growing CNTs with non-iron metallocene
- Bond Strength between CNTs and the Fibers
- Conclusions

Outline

- Background
- The innovation
- Mechanical Properties Characterization
- Growing CNTs with alternative metallocene with transition metals
- Bond Strength between CNTs and the Fibers
- Conclusion and future research

Interphase in Composites

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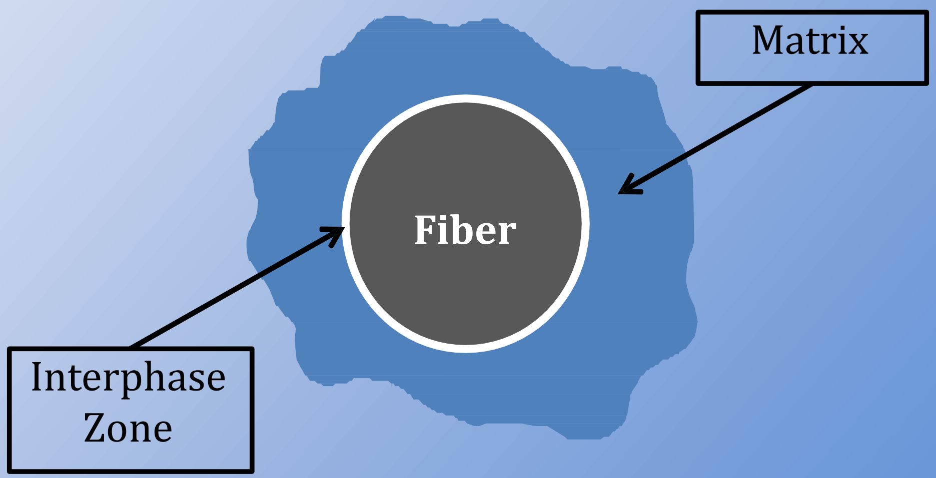
- Fiber reinforced polymers (FRPs) consist of three main components:
  - Reinforcing materials
  - Matrix
  - Interphase zone
- Fiber dominated properties are advantageous
- Matrix and interphase zone - dominated properties present undesirable features within FRPs



Why CNT Reinforcement?

- ✓ Extraordinary mechanical properties
  - ▪ have the potential to produce much stronger and tougher materials than traditional reinforcing materials. CNT reinforcements have the potential to produce much stronger and tougher materials than traditional reinforcing materials
- ✓ Excellent thermal and electrical properties
  - ▪ provide materials with functional advantages such as
    - o self-sensing abilities, flame retardancy,
    - o wear resistance,
    - o electrical and thermal conductivity,
    - o electromagnetic interference shielding,
    - o improved thermal stability

CNT Synthesis

There are numerous existing methods used to synthesize CNTs for use in composites.

- Chemical vapor depostion (CVD) method
  - Requires high reaction temperature (650° C - 1050° C) in a closed chamber
  - Requires feedstock gases , inert gas protection
  - Produces high-quality CNTs
  - Can reduce tensile strength of fibers up to 50%
  - Difficult to scale up
- Various other methods that deposit CNTs onto fibers, using:
  - Electrophoretic deposition
  - Dip coating
  - Nanocomposite polymer sizing

CNT Implementation

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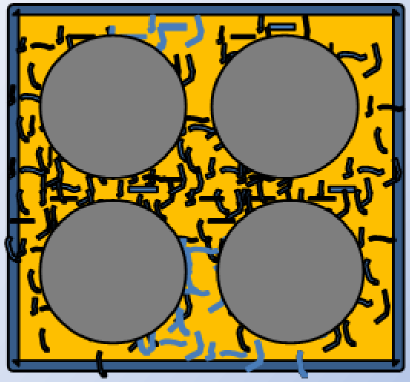
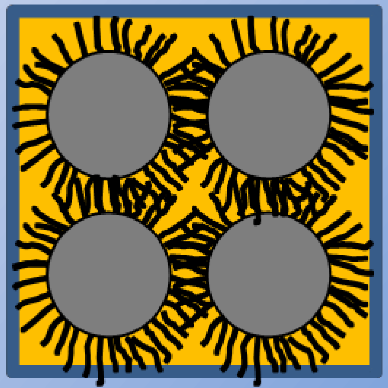
- Implementation of CNTs into composites is generally difficult.
- Two basic reinforcing schemes:
    1. Direct dispersion of CNTs into the matrix
    2. CNTs grown directly on fibers/fabrics



Direct dispersion of CNTs into matrix



CNTs grown directly on fibers/fabrics

Motivation

CNT Synthesis

•Existing CNT synthesis methods are generally:

- Difficult to carry out
- Difficult to scale (prevents commercial end users from adopting)
- Prone to excessive fiber damage

CNT Implementation

•Direct dispersion:

- Allows for scalability
- Leads to difficulty in composite manufacturing (viscous matrix material + nano-sized particles)

•CNTs grown directly on fibers/fabrics avoids the difficulty inherent with direct dispersion

Objective

Develop a scalable, low-cost technique to grow CNTs on microfibers and use this method to manufacture structural composites with enhanced mechanical performance and durability.

The Innovation

- Background
- The innovation
- Mechanical Properties Characterization
- Growing CNTs with non-iron metallocene.
- Bond Strength between CNTs and the Fibers
- Conclusion and future research

Poptube Technology-Working Principle

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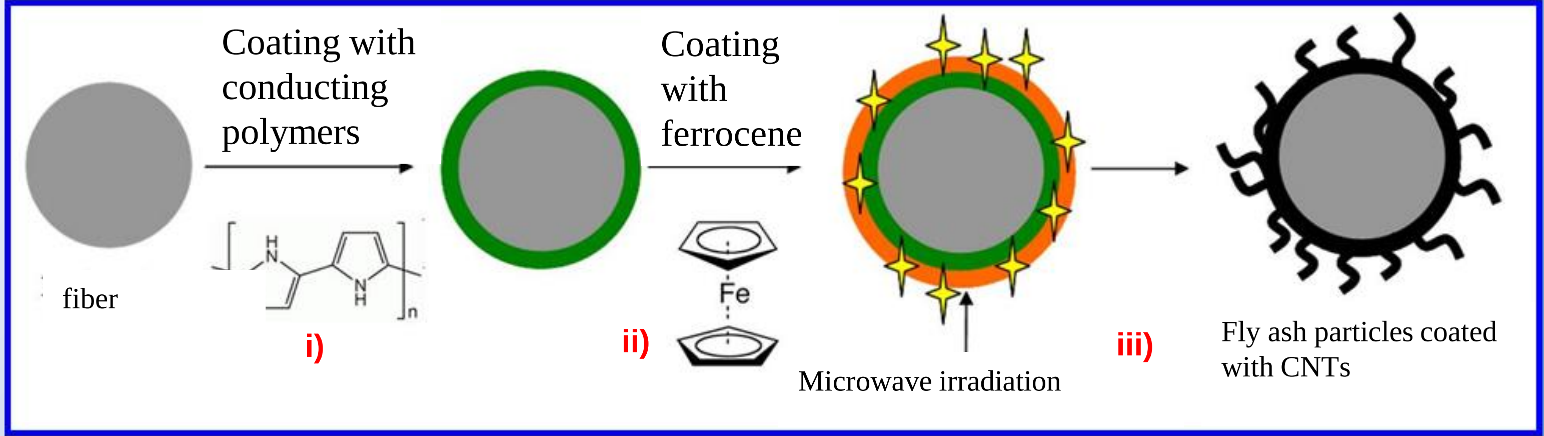
- ✓ Three elements in manufacturing CNTs:
  - Reaction temperature, carbon source, and catalyst
- ✓ Poptube Technology:
  - Reaction temperature – microwave heating
  - Carbon sources and catalyst - ferrocene



Growing CNTs on a Fiber Using Poptube Technology

CNTs Grown On Fly Ash And Glass Fabrics

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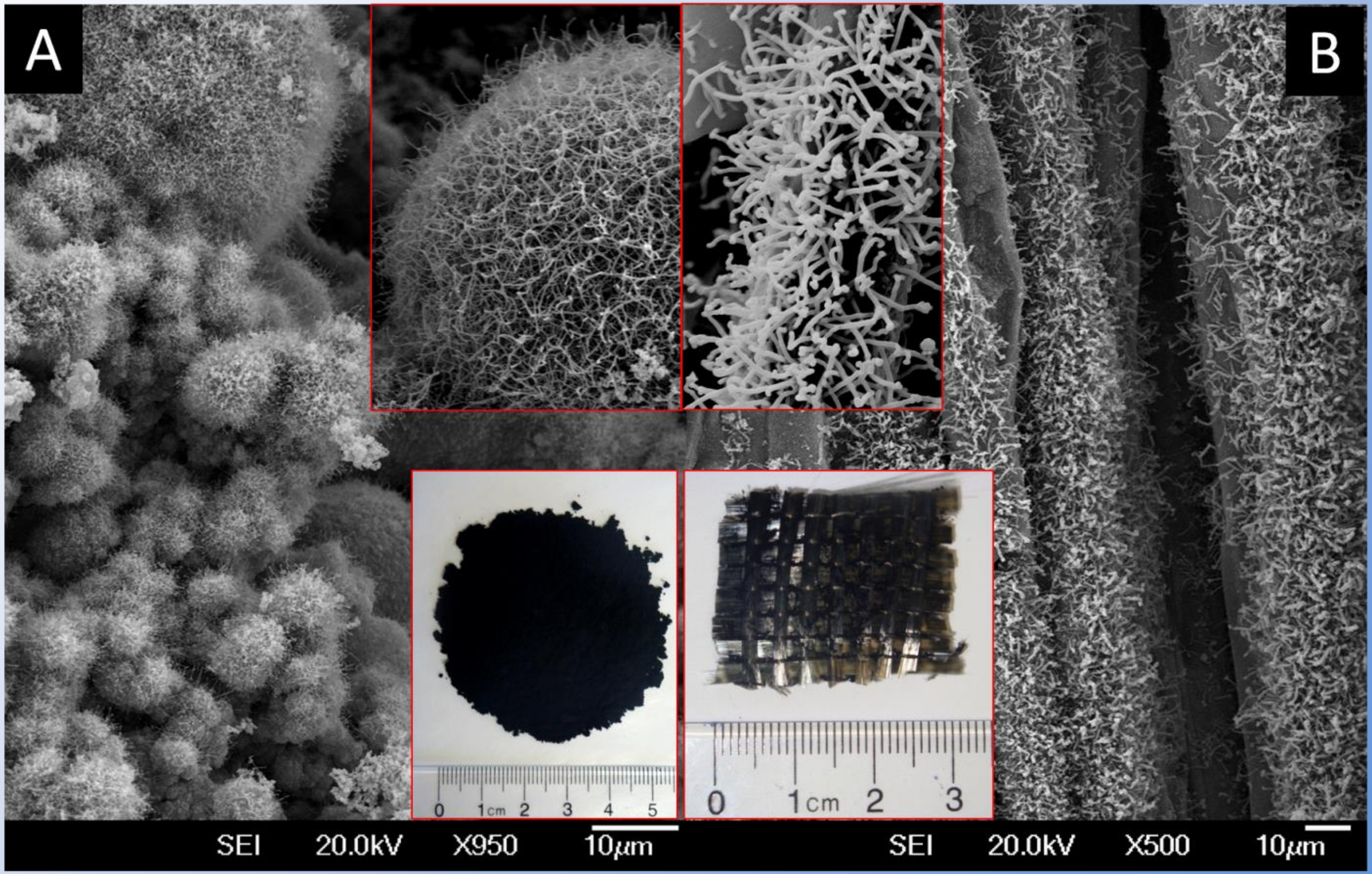

Fig 3. SEM images of as produced CNTs on (A) fly ash, insets: (top) zoom-in SEM image of the CNTs on fly ash; (bottom) digital picture of 10 g fly ash-CNT nanocomposite; and (B) glass fiber fabrics, inset: (top) zoom-in SEM image of the CNTs on glass fiber fabrics; (bottom) digital picture of 1 inch × 1 inch glass fiber fabric-CNT nanocomposite.

HTEM Image of Produced CNTs

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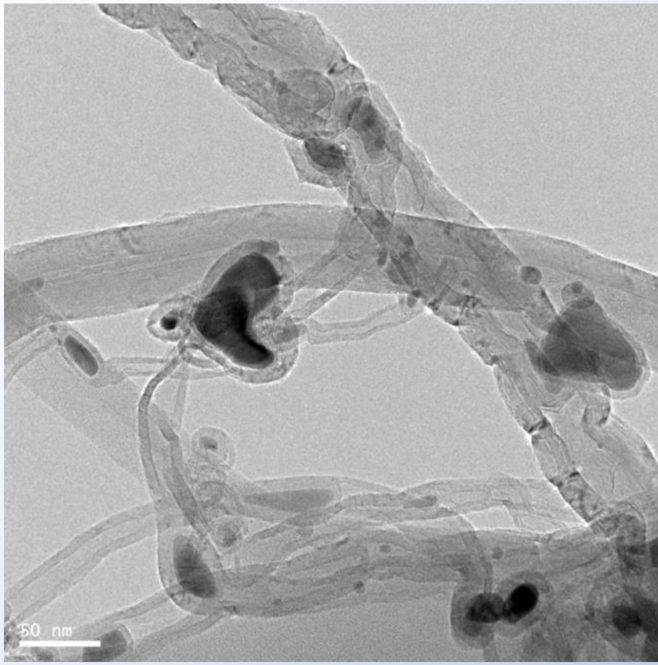


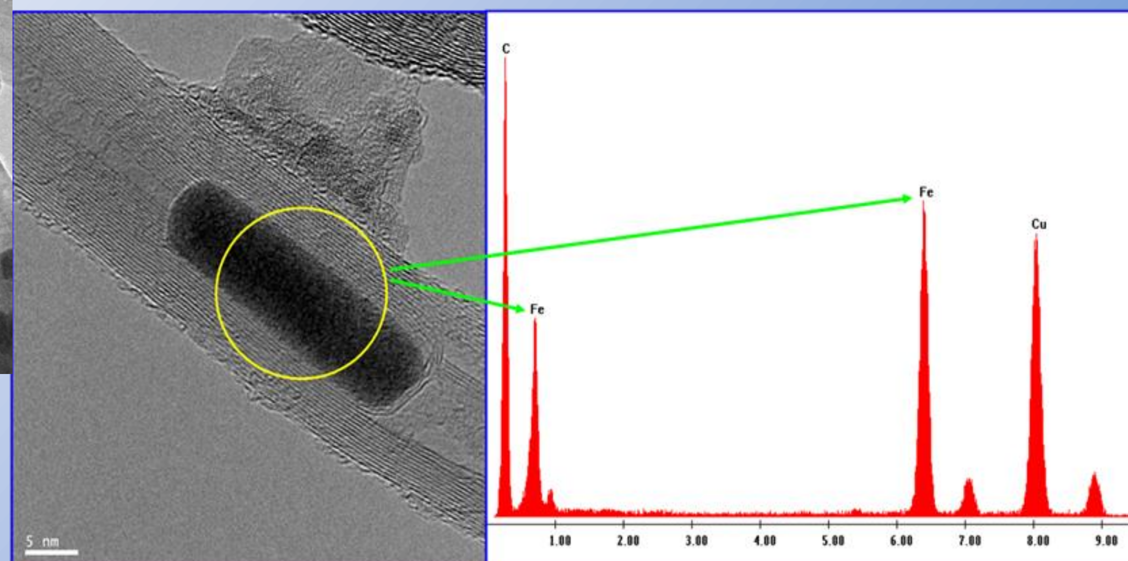
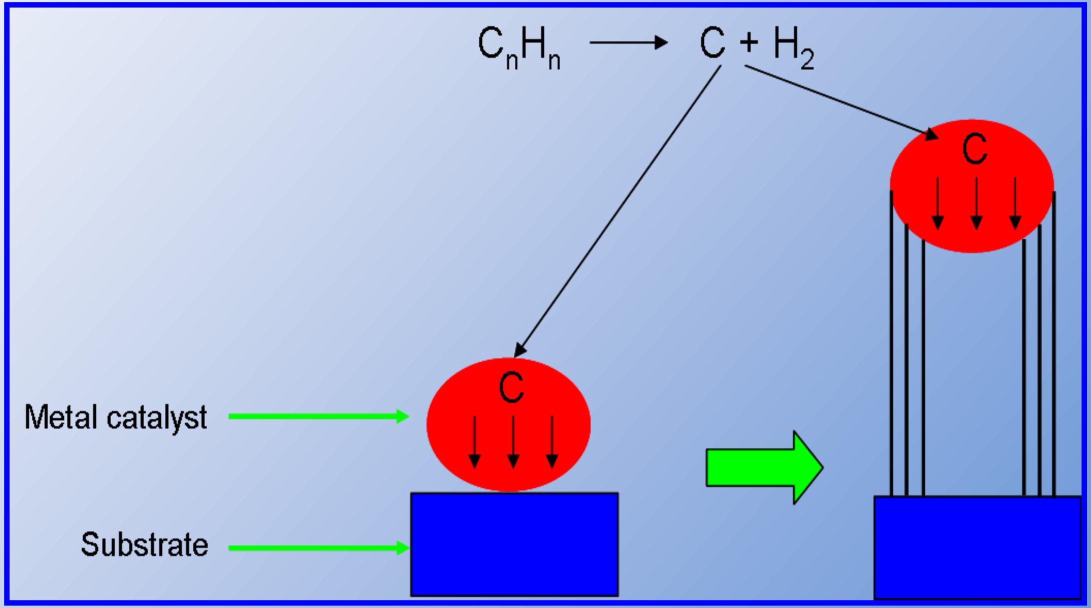


Fig 5. HRTEM image of the as-produced CNTs and EDX on selected area

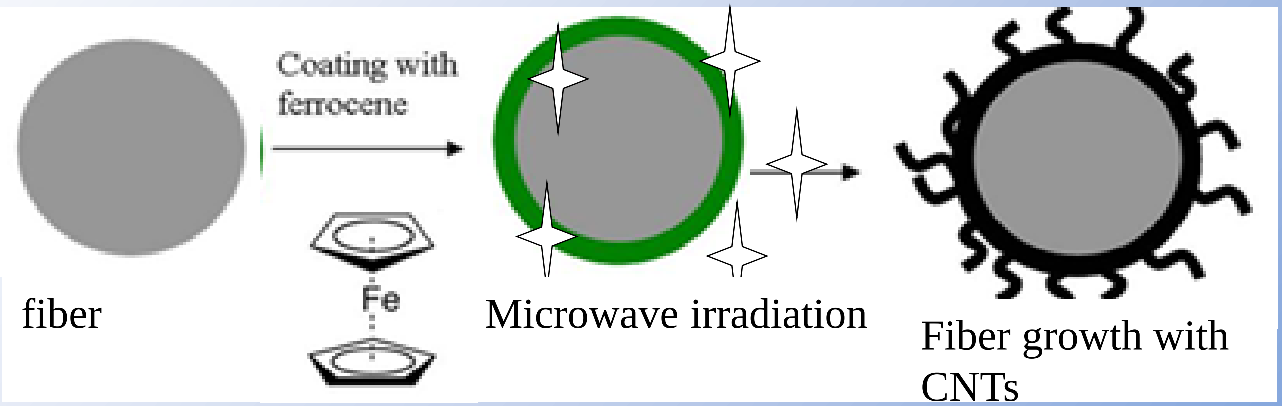
Growth Mechanism Of CNTs

i) upon microwave heating, the conducting layer will absorb the microwave irradiation;
ii) the temperature will rise up very quickly and reach high enough to decompose ferrocene to iron and cyclopentadienyl groups.



iii. iron will stick on the surface of the heating layer, and serve as the catalyst.
iv. the carbon atoms pyrolyzed from cyclopentadienyl ligand will serve as the carbon source.

The PopTube technology-Carbon Fibers



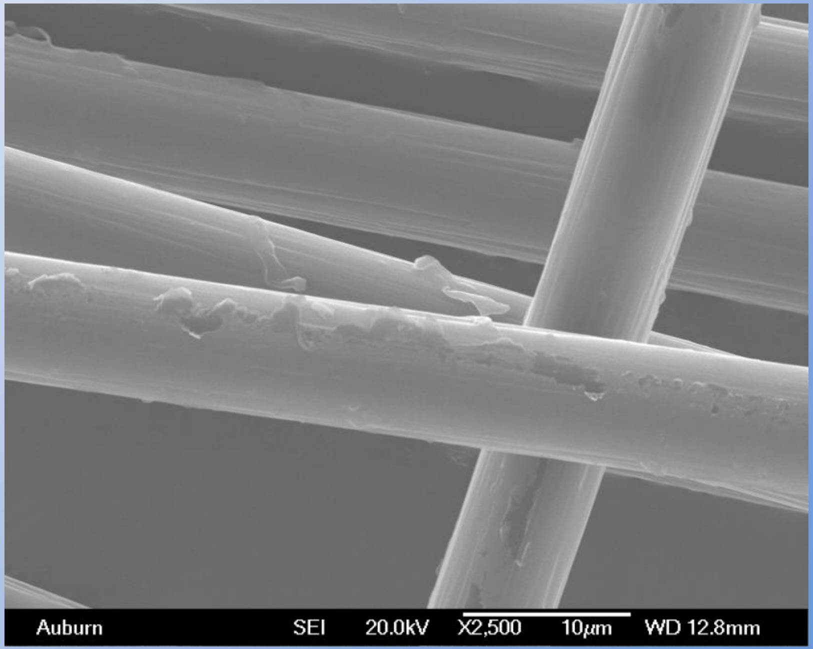
Since carbon fiber can absorb microwave energy. Conducting polymer is not needed to grow CNTs on carbon substrates! The proposed technique has been significantly simplified.

Key Advantages

- PopTube Technology requires very simple, commonly available equipment
  - Lends itself to large scale, high yield manufacturing
- PopTube Technology is highly energy efficient
  - Very low energy consumption compared to existing methods
- PopTube Technology is very cost effective
  - Only inexpensive chemicals are required
  - No need for expensive feedstock gases
- PopTube Technology allows for continuous manufacturing

Control of CNTs Growth– Pretreatment

- ✓ Virgin CF Fabric – no treatment
- ✓ Microwave Pretreatment
  - Virgin CF fabric exposed to microwave irradiation for 1 min
- ✓ Acetone Pretreatment
  - Virgin CF fabric soaked overnight in acetone



SIGMATEX carbon fiber fabric: DV 233, Plain weave,195 g/sq.m, with silane sizing layer

Control of CNTs Growth -Processing

- ✓ After pre-treatment, CF Fabric soaked for 30 min in a 0.5M Ferrocene-Toluene solution.
- ✓ Fabric removed from the solution and allowed to dry.
- ✓ Sample was microwaved for 45 sec.
- ✓ Hexane addition
  - Before MW, 1 mL of hexane (0.5 mL on each side of fabric) was added to 1 sample from each set (No PT, MW PT, Acetone PT)

No Pretreatment- Carbon Fiber Fabric

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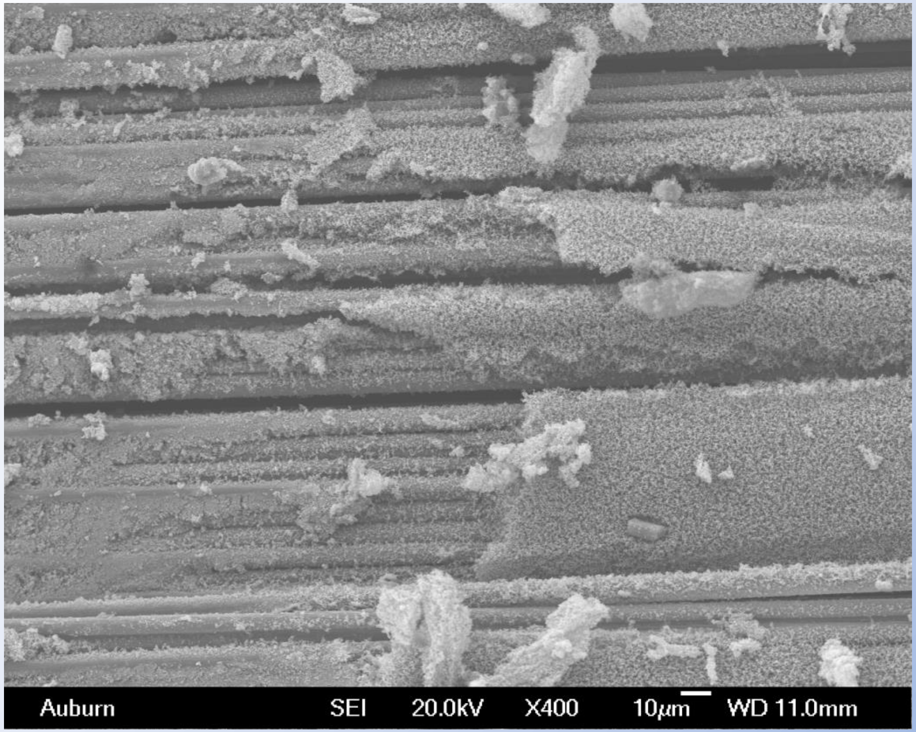

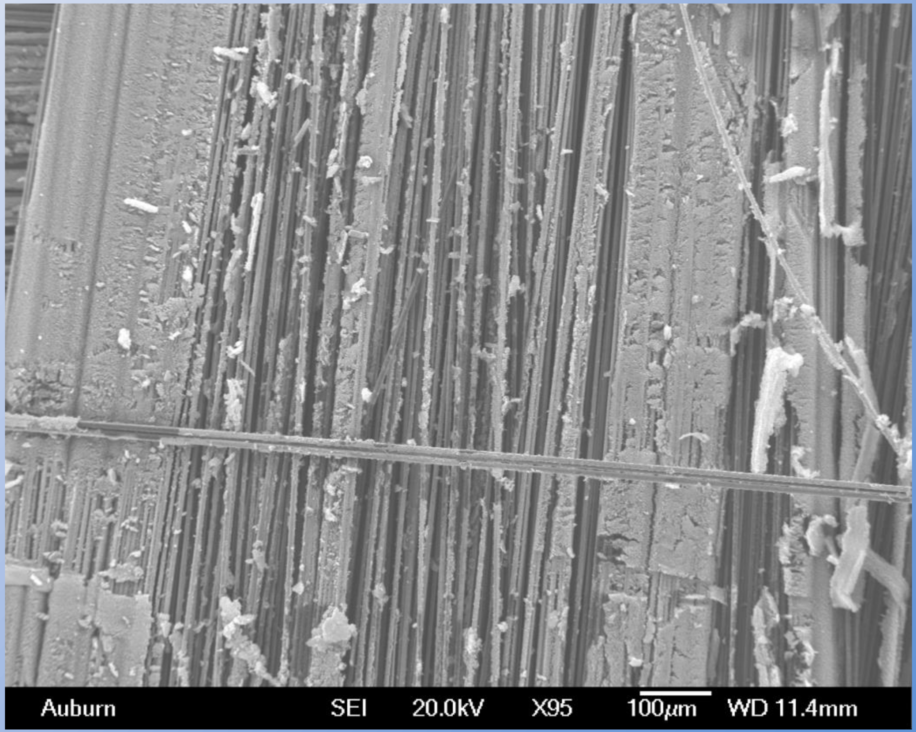

Areas of decent coverage, yet on a larger scale the coverage is relatively poor and non-uniform.

No Pretreatment-Carbon Fiber Fabric with Hexane

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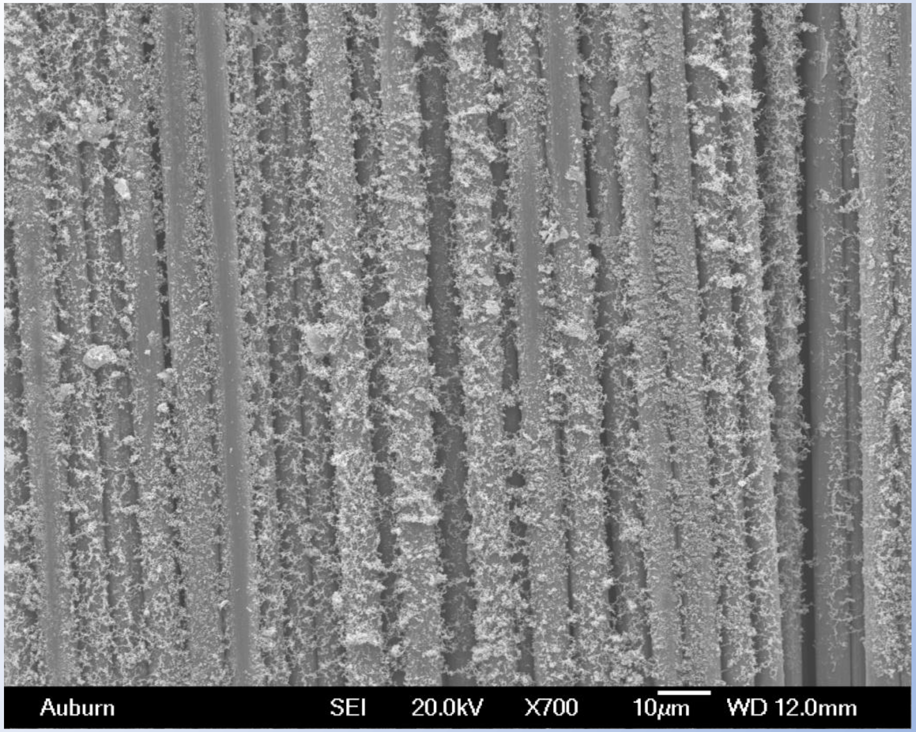

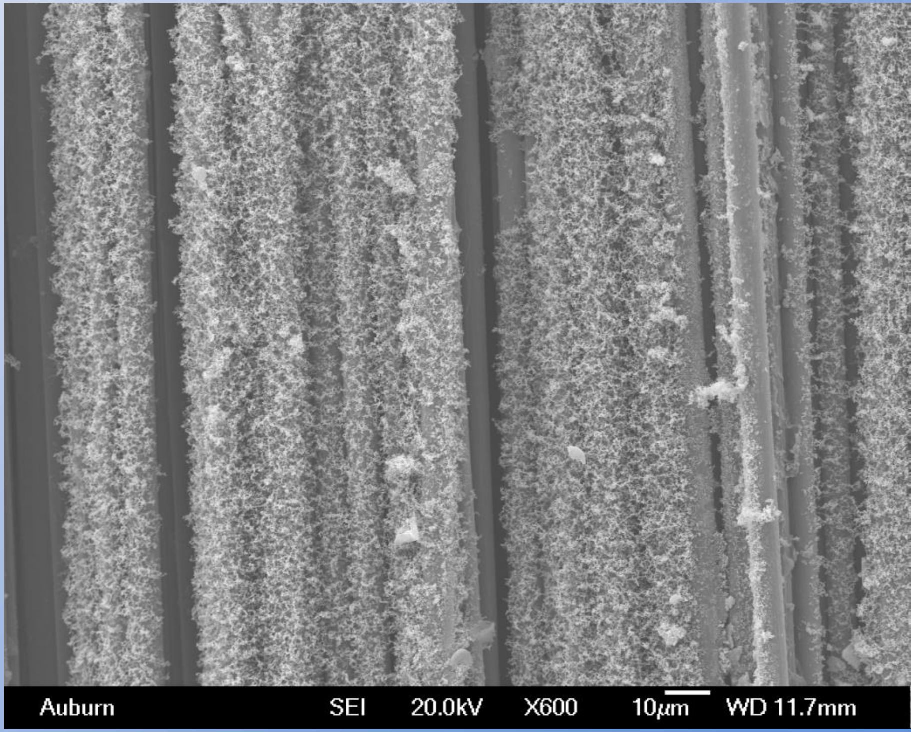

The addition of hexane improves the coverage on the CF

Microwave Pretreatment- Carbon Fiber Fabric

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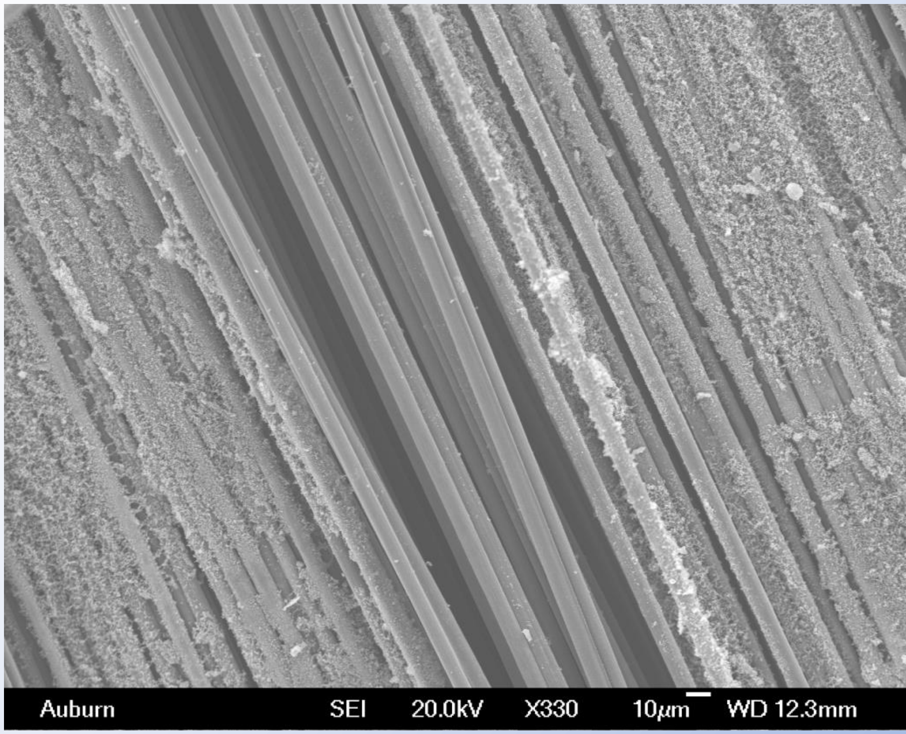
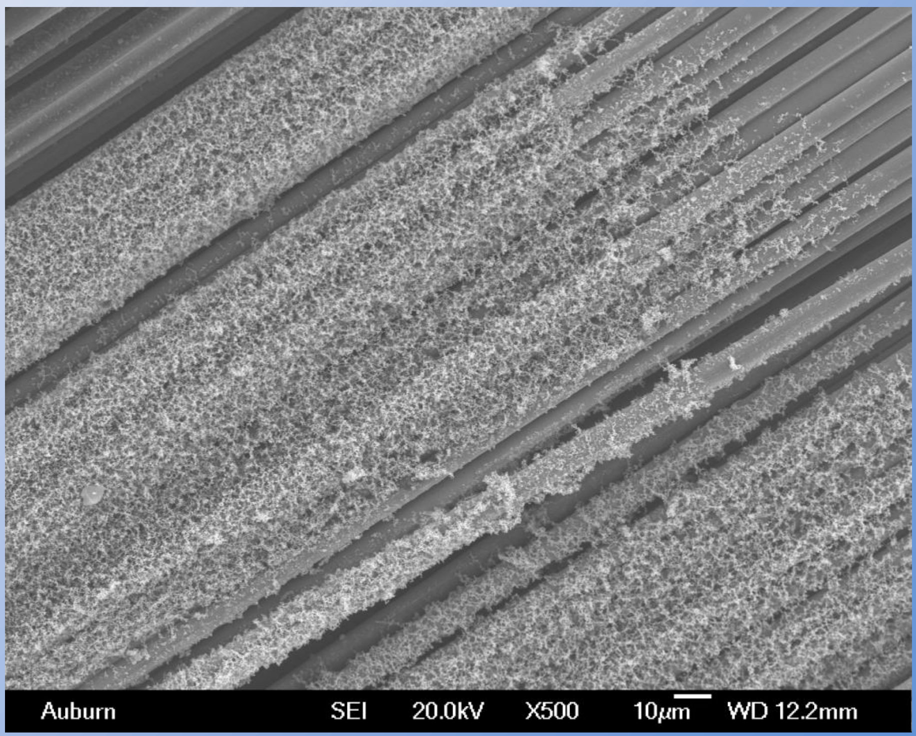
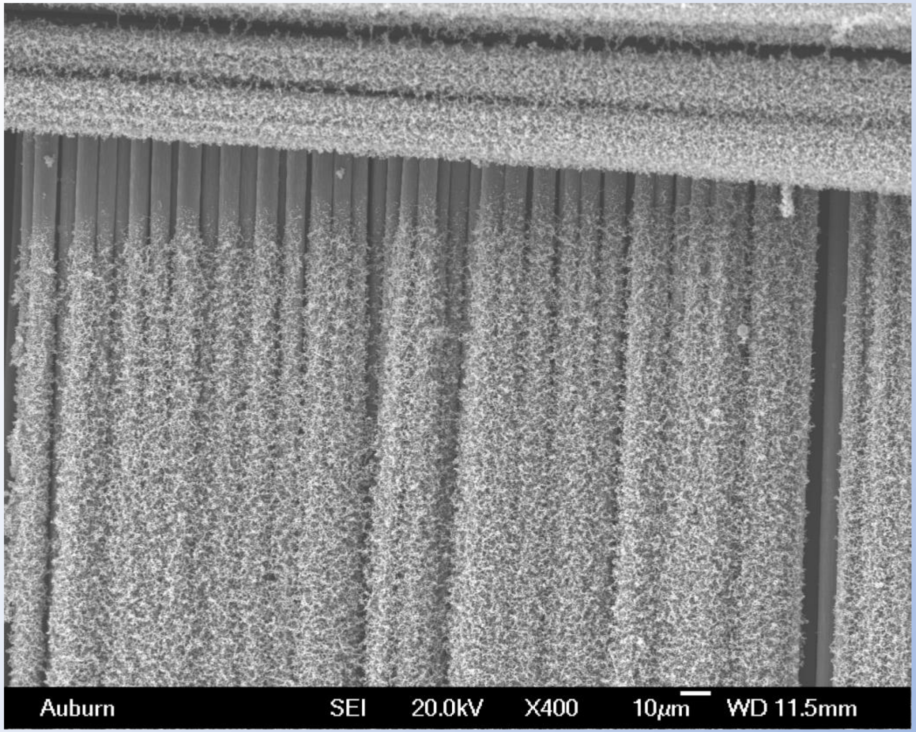
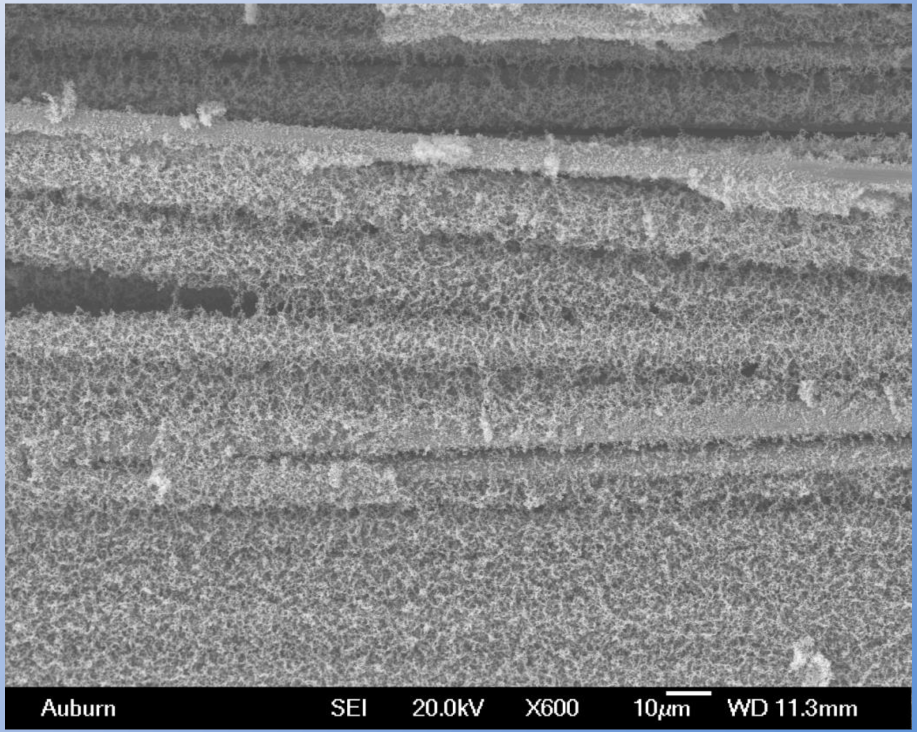




MW pre-treatment provides a much cleaner surface for attachment that translates to a better coverage and growth compared to the sample without pre-treatment.

Microwave Pretreatment- Carbon Fiber Fabric w/ Hexane





The addition of hexane improves the coverage on the MW Carbon Fiber

Acetone Pretreatment-Carbon Fiber Fabric

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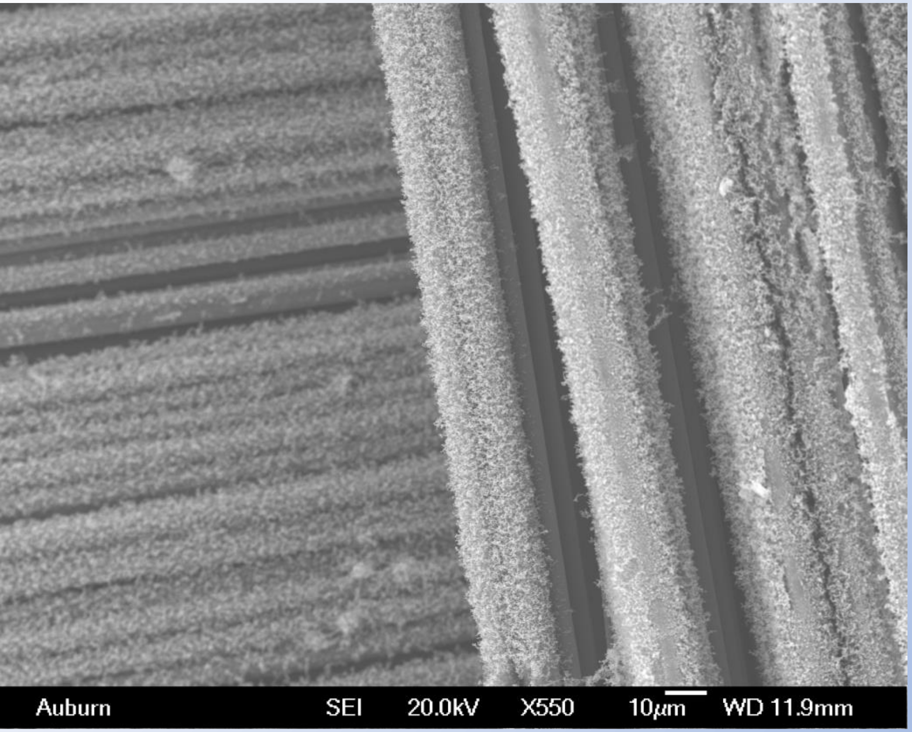

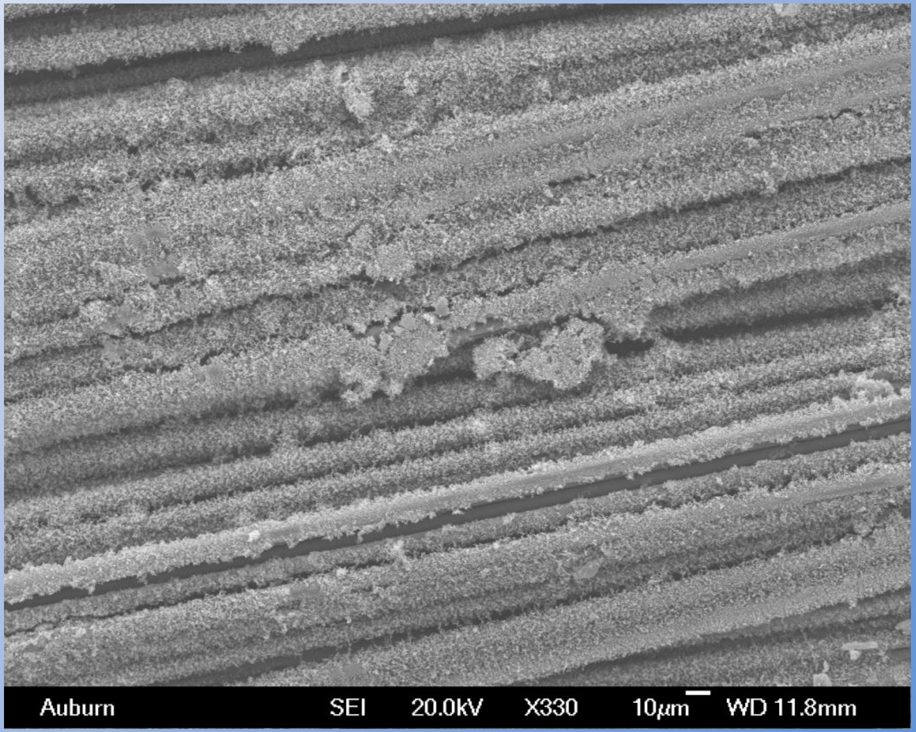

This sample provides the best growth and coverage for samples that do not have the addition of hexane.

Acetone Pretreatment- Carbon Fiber Fabric w/ Hexane

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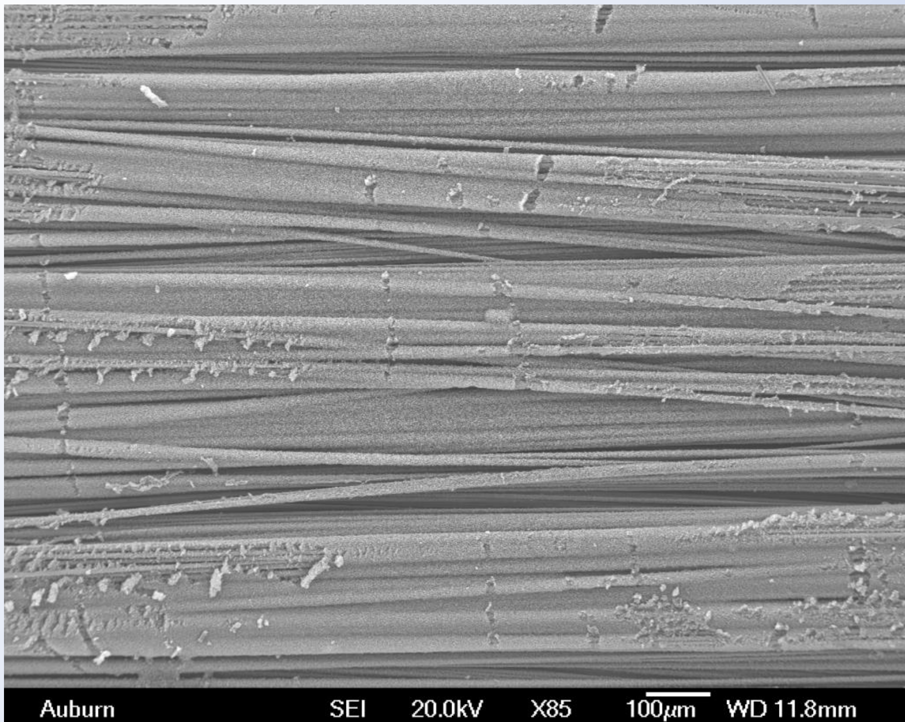

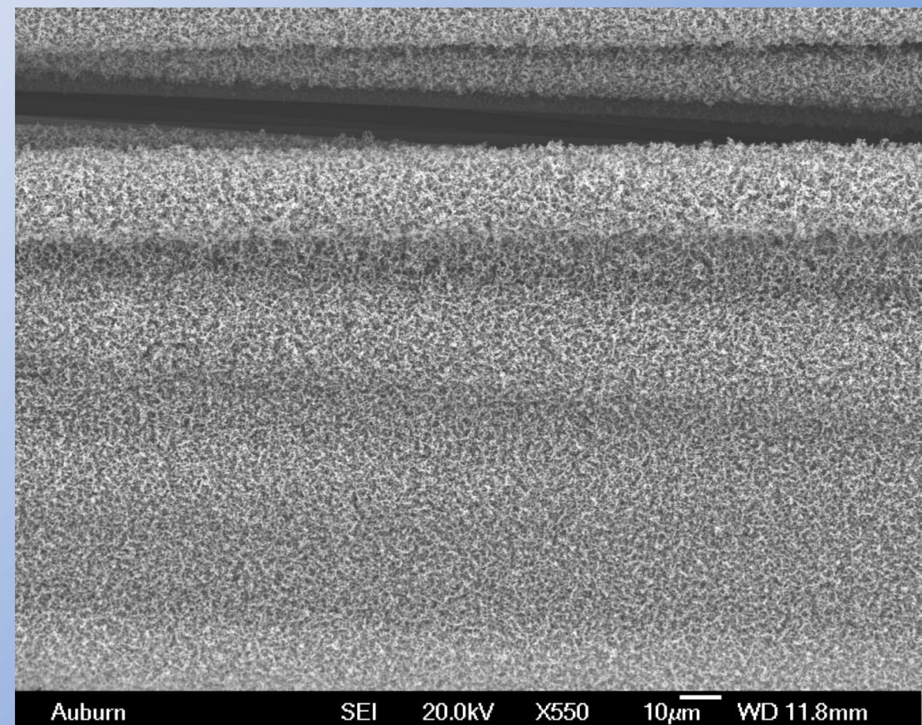

- The addition of hexane improves the coverage on the CF
- The best coverage in terms of uniformity

Mechanical Properties Characterization

- Background
- The innovation
- Mechanical Properties Characterization
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- Bond Strength between CNTs and the Fibers
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Single Fiber Tension Test

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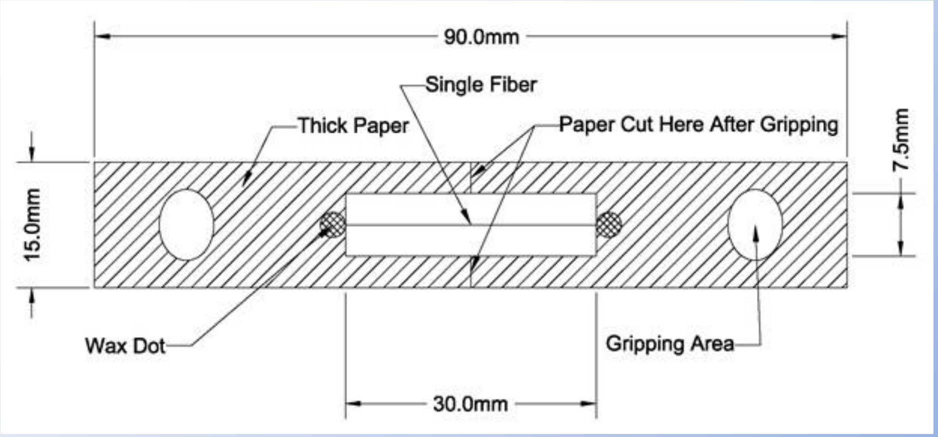
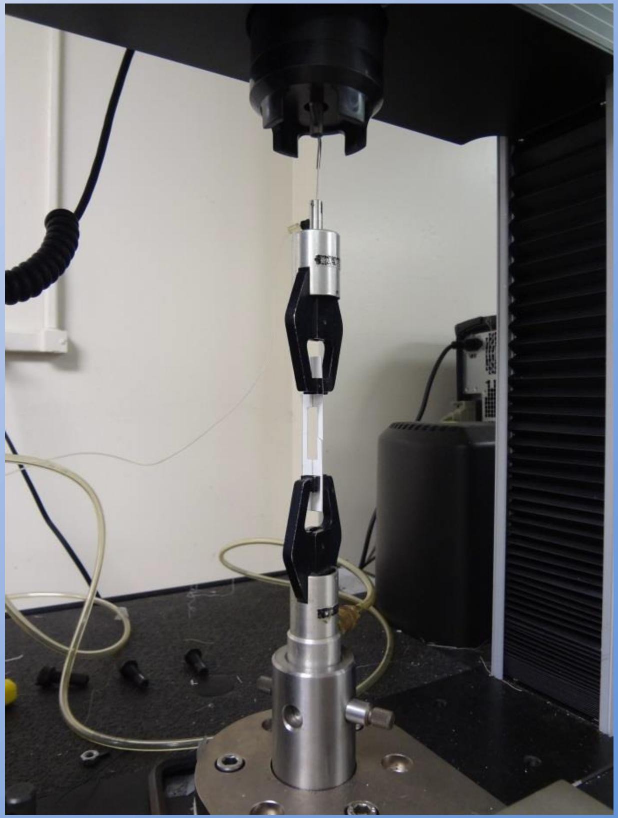
- Determine whether PopTube Technology induces significant damage in the fibers
- Performed on individual carbon fibers (virgin and PopTube Technology- treated) according to ASTM D 3379





Single Fiber Tension -Result

Single fiber tensile test results.				
Test Group	Weibull Parameters		Strain-to-Failure (mm/mm)	Axial Young's Modulus (GPa)
	Weibull modulus, m	Characteristic strength, σ_0 (MPa)		
Virgin (without CNTs)	8.65	3725	.01957 ± .00259	226.7 ± 11.3
PopTube Technology (with CNTs)	4.34 (-49.8%)	3301 (-11.4%)	.01728 ± .00426 (-11.7%)	218.2 ± 14.2 (-3.76%)

- PopTube Technology CNT synthesis process leads to
  - 10% reduction in single fiber tensile strength
- Weibull analysis suggests that due to PopTube Technology:
  - Number of flaws present in fibers increases (m)
  - Size of flaws present in fibers increases (σ_0)

Composite Tension Test

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- Determine how fiber damage from CNT synthesis manifests itself at the composite scale.
- Performed on carbon fiber laminate composites (virgin and PopTube Technology-treated) according to ASTM D 5528.
- 5”x1” coupons loaded in tension to failure.
- Strains measured via digital image correlation (DIC).

Uni-axial Tensile Test Results

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Test Group	Strength (MPa)	Strain-to-Failure (mm/mm)	Tensile Chord Modulus (GPa)	Poisson's Ratio	
Virgin (without CNTs)	778.0 ± 15.9	.01193 ± .000197	63.46 ± 2.20	.0627 ± .021	
PopTube Technology (with CNTs)	555.9 ± 44.7 (-28.5%)	.009413 ± .00103 (-21.1%)	59.89 ± 2.94 (-5.63%)	.0599 ± .016 (-4.45%)	

- The declines in tensile strength and strain-to-failure can be attributed to several different contributing factors:
  - fiber damage induced by CNT growth composite manufacturing (fibers without sizing used) .
  - a reduction in fiber volume fraction due the presence of CNTs on the fibers (which was measured for both test groups using an optical imaging Technology)
  - change in tensile failure mode due to the presence of CNTs on the fibers.

Failure Mode

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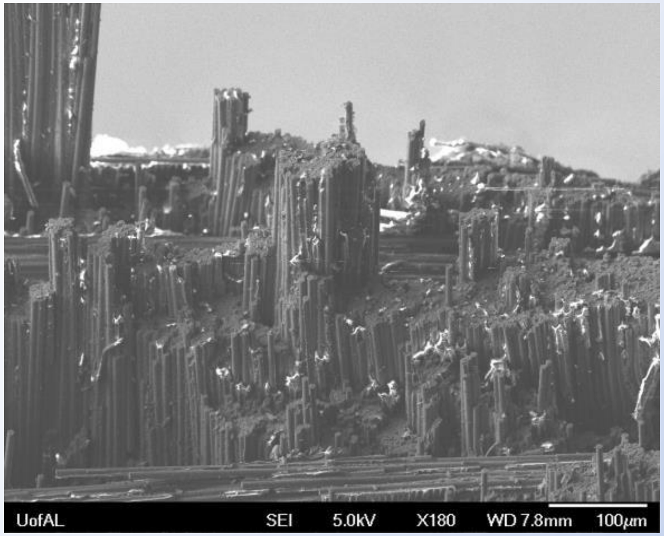
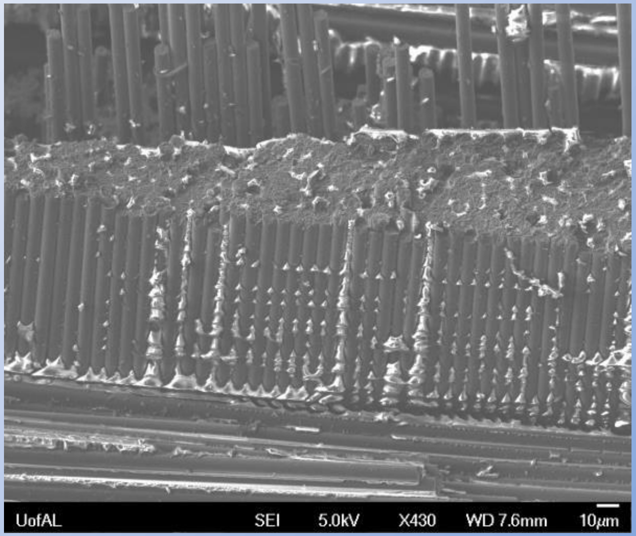


Virgin



PopTube Technology

Composites treated by PopTube Technology:

Transverse cracks cut perpendicularly across the longitudinal fibers, leaving behind a relatively flat and clean fracture surface, indicating

- little to no cracking parallel to the longitudinal fibers, suggesting strong fiber-matrix interface not allowing for fiber-matrix debonding to occur.
- the “crack arresting” mechanism offered by fiber-matrix debonding was not operative.
- no means of stress relief is readily available for critically-stressed regions, leading to a less uniform distribution of stress across the composite and local high stress “hot spots”.

Mitigation of Tensile Strength Reduction

- Unsized carbon fibers were used to grow CNTs.
- Extra damage can be induced to the fibers during the manufacturing of the composite samples using hand layup.
- By applying sizing to carbon fibers after growing CNTs, less damage can be induced by handling of carbon fibers.
- A polyurethane-based sizing agent designed for use with epoxy matrix materials – Hydrosize U6-01 (manufactured by Michelman) was used.

Effect of Sizing

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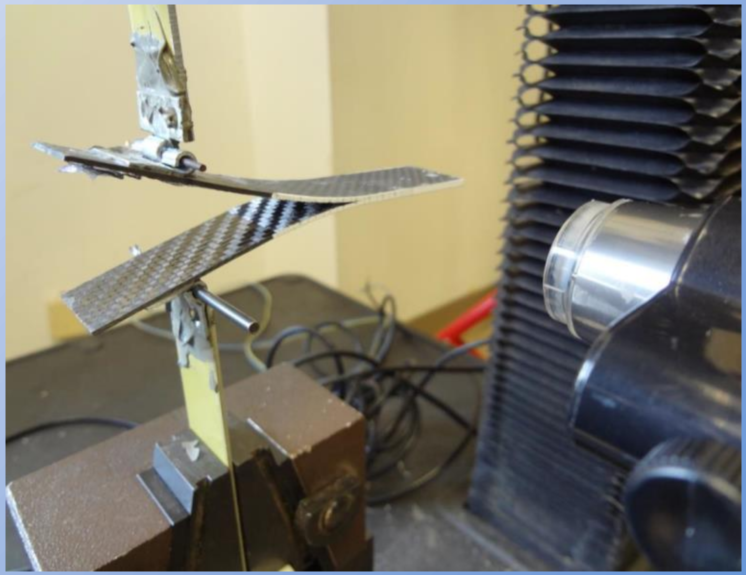
Uni-axial composite tensile test results.					
Test Group	CNTs?	Sizing?	Strength (MPa)	Strain-to-Failure (mm/mm)	Tensile Chord Modulus (GPa)
1	No	No	778.0 ± 15.9	.01193 ± .000197	63.46 ± 2.20
2	Yes	No	592.4 ± 69.3	.00969 ± .00128	59.89 ± 2.94
Relative Difference			-23.9%	-18.8%	-5.63%
p-value			.000	.068	.023
3	No	Yes	751.9 ± 73.5	.01264 ± .00163	
Relative Difference			-3.36%	+5.95%	
p-value			.207	.036	
4	Yes	Yes	708.7 ± 64.0	.01381 ± .00240	
Relative Difference			-8.91%	+15.7%	
p-value			.012	.070	

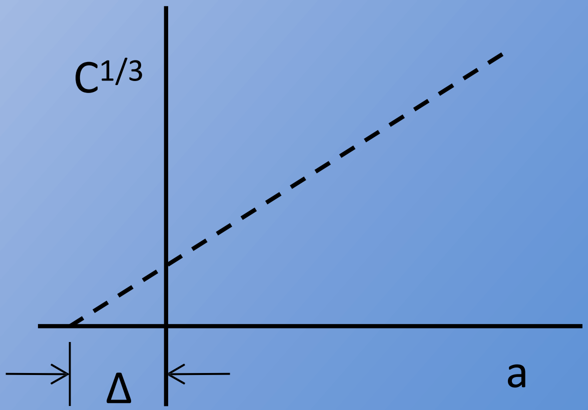
The CNT-reinforced group with sizing showed a markedly smaller reduction in strength compared the CNT-reinforced group without sizing.

Mode I Fracture Testing

- Determine whether the PopTube Technology improves Mode I delamination resistance in composites.
- ASTM D5528
- Specimen loaded in tension such that crack is allowed to grow 40-50 mm total
- mode I fracture toughness calculated via Modified Beam Theory (MBT):

$$G_I = \frac{3P\delta}{2b(a+|\Delta|)}$$



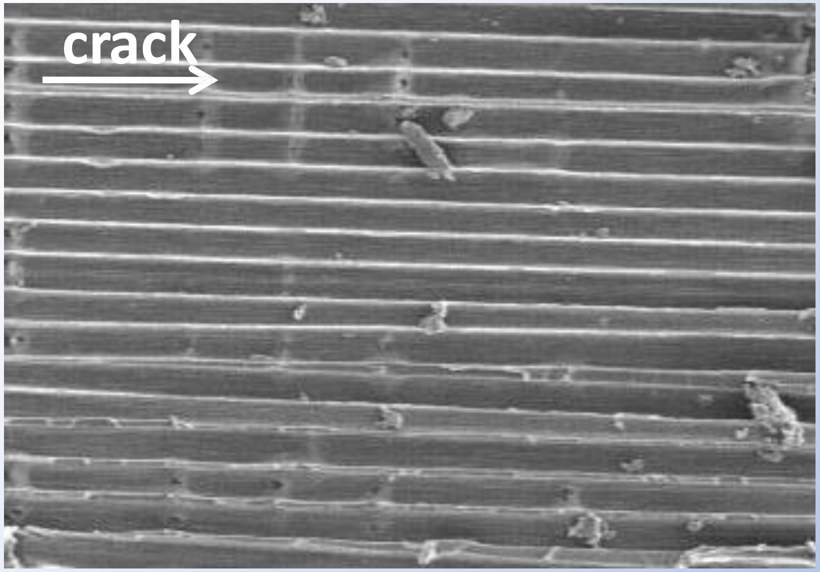


Measured Mode I Fracture Toughness

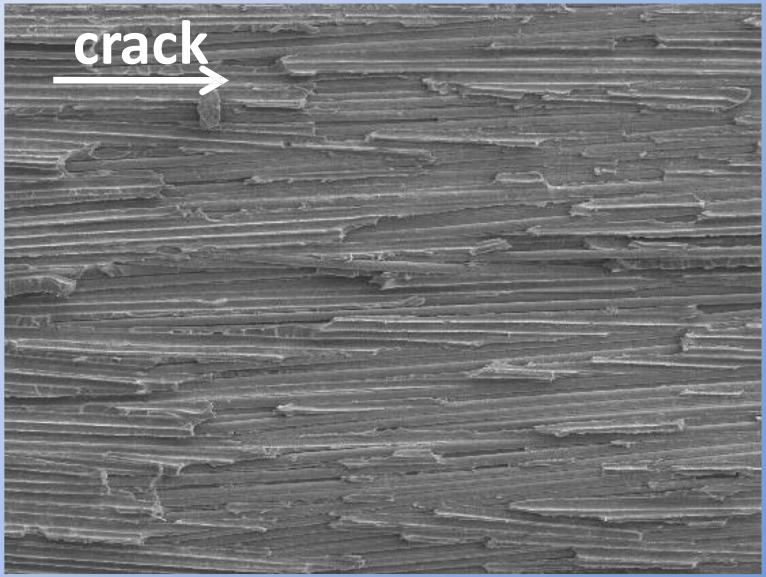
Double cantilever beam test results.			
Test Group		Mean Mode I Fracture Toughness, G_{Ic} (kJ/m^2)	
		NL	VIS
Modified Beam Theory	Virgin	0.21±.03	0.35±.11
	Treated	0.29±.12 (+36%)	0.53±.19 (+48%)
Modified Compliance Calibration	Virgin	0.22±.03	0.35±.10
	Treated	0.29±.11 (+41%)	0.52±.19 (+48%)

PopTube Technology-treated composites showed significant improvements in Mode I fracture toughness upon crack initiation.

Fractography



Virgin



PopTube Technology

Rough matrix cohesive failure indicating a strong fiber/matrix interfacial bond, leading to higher fracture toughness

Mode II Fracture Toughness

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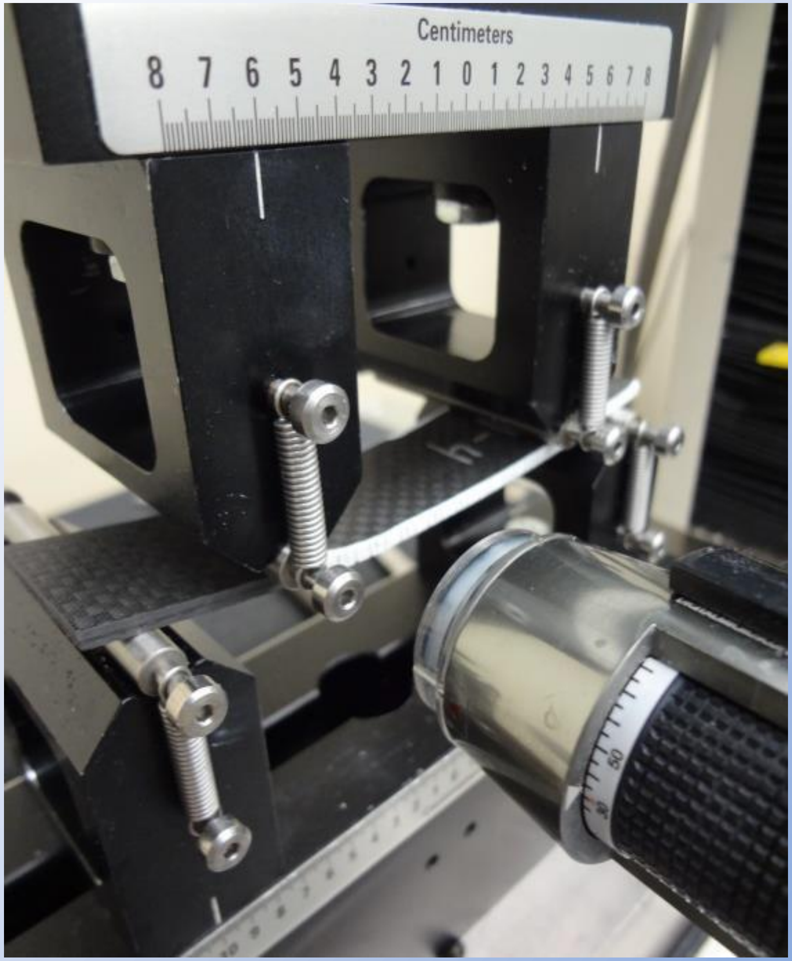
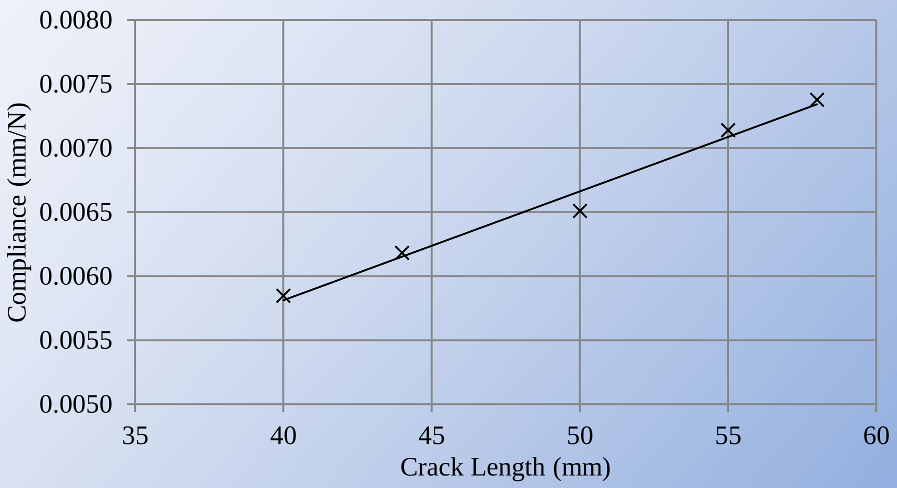


- Determine whether PopTube Technology improves Mode II delamination resistance in composites.
- Four point end-notched flexure (4ENF)
- Specimen loaded/unloaded in bending such that crack is allowed to grow 3-5 mm each cycle (25-50 mm total)

Mode II Fracture Toughness



Test Group	Mode II Fracture Toughness (kJ/m2)
Without CNTs	0.767 ± 0.072
With CNTs	0.824 ± 0.110
Relative Difference	+7.34%
p-value	.016

Mode II Fractography

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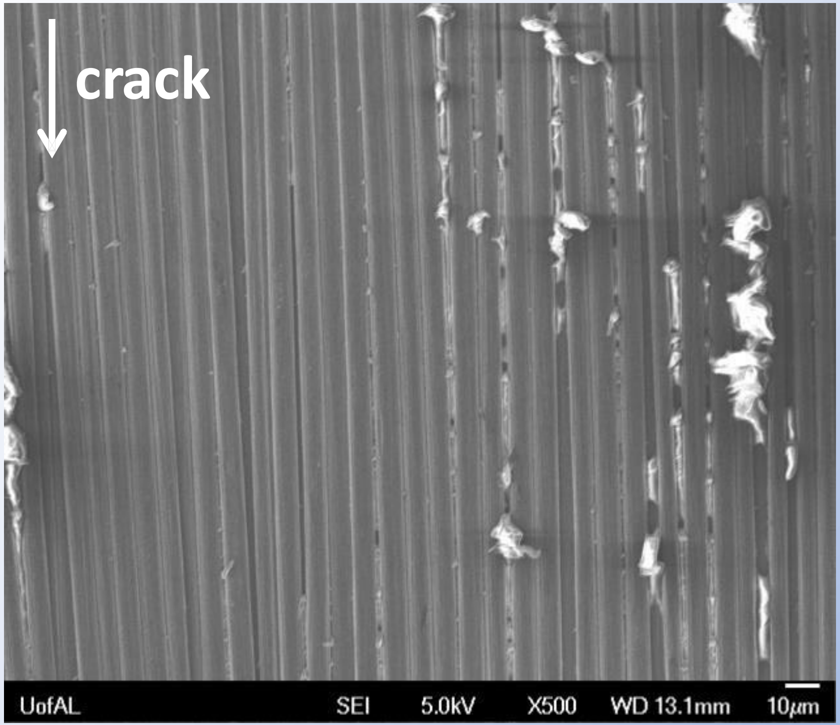
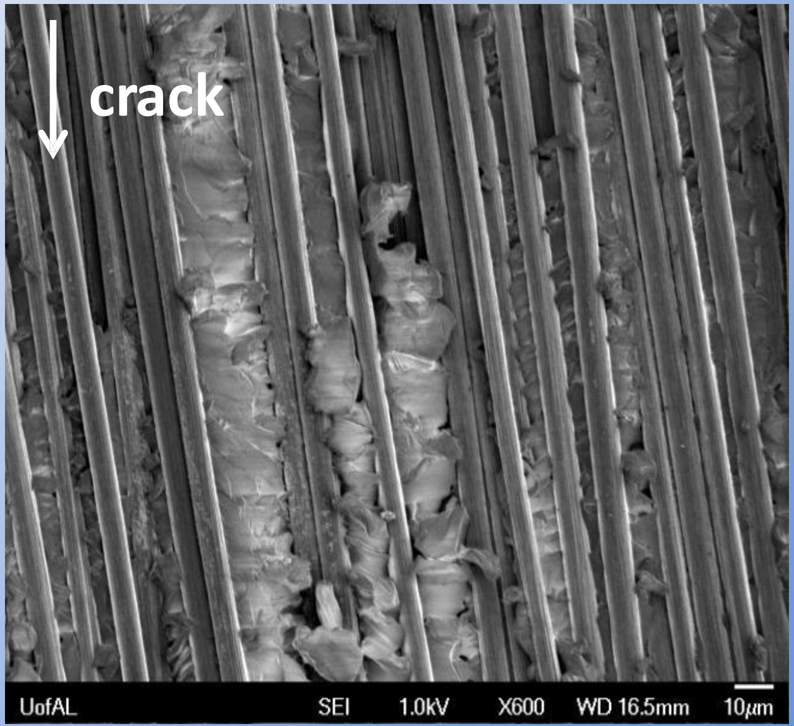


Virgin



PopTube Technology

- CNTs have a positive effect on fiber-matrix adhesion.
- Dominant failure modes due to Mode II loading are fiber-matrix interface failure and cohesive matrix failure

Short-Beam Test

Determine whether the PopTube Technology reinforces improves interlaminar shear strength in composites

Specimen Geometry

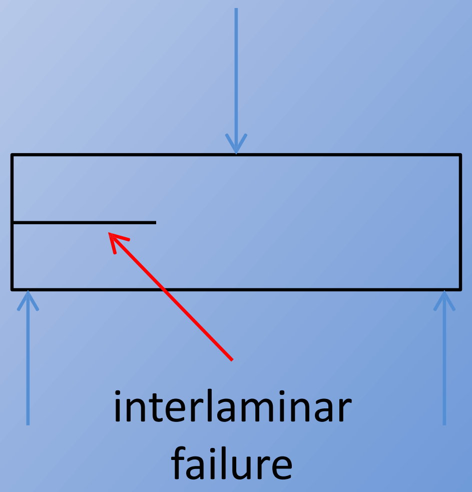
•Per ASTM D2344

•3.5 mm thick x 7.0 mm wide

•Span length: 25.4 mm

•Load composite beams to failure in three- point bending

•Calculate short-beam strength, F^{sbs}



$$F^{sbs} = 0.75\frac{P_m}{bh}$$

Interlaminar Shear Strength

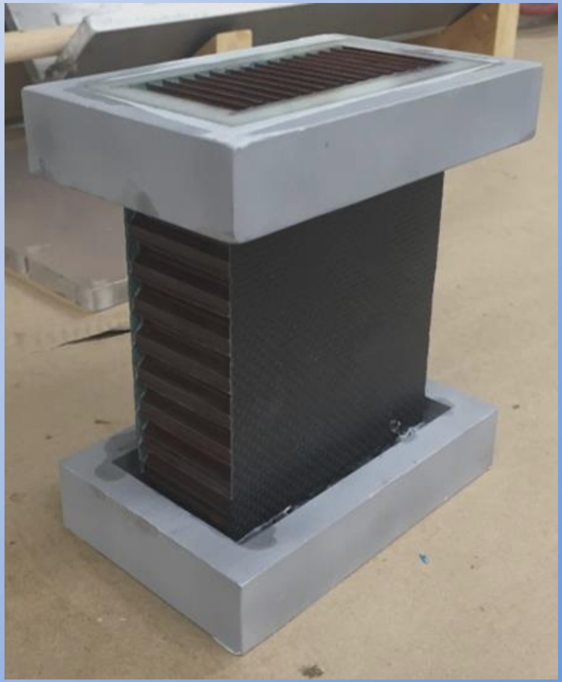
Short-beam shear test results.

Group	Max Load, P_{max} (N)	Cross-Section Area, bh (mm^2)	F^{sbs} (MPa)
Virgin (without CNTs)	622.9 ± 62.5	22.8 ± 0.75	20.49 ± 1.65
Treated (with CNTs)	940.1 ± 11.0 (+50.9%)	26.2 ± 0.51 (14.9%)	26.96 ± 0.70 (+31.6%)

- PopTube Technology significantly enhances interlaminar shear strength
  - 30% improvement in short-beam shear strength

Drop-Weight Impact/CAI

- Determine whether PopTube Technology improves damage tolerance in composites.
- To accommodate eventual compression loading, sandwich panel specimens were used in lieu of thick, monolithic composites.
- Sandwich panel specimens potted in aluminum frames to allow for compression loading and prevent end-brooming.



Drop-Weight Impact

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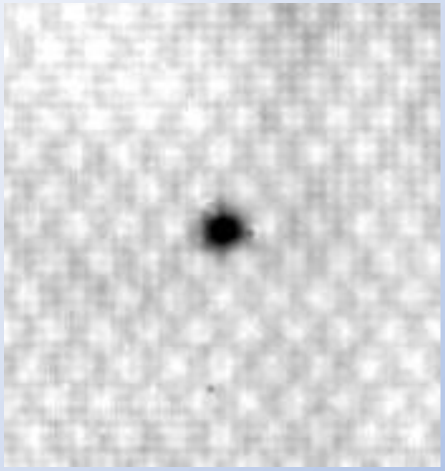

- A hemispherical striker with a diameter of 6.35 mm (0.25 in.) was used to impact the composite laminate facesheets.
- A Thermal Wave Imaging EchoTherm infrared thermography analysis system was used for estimated damage dimension

Compression After Impact (CAI)

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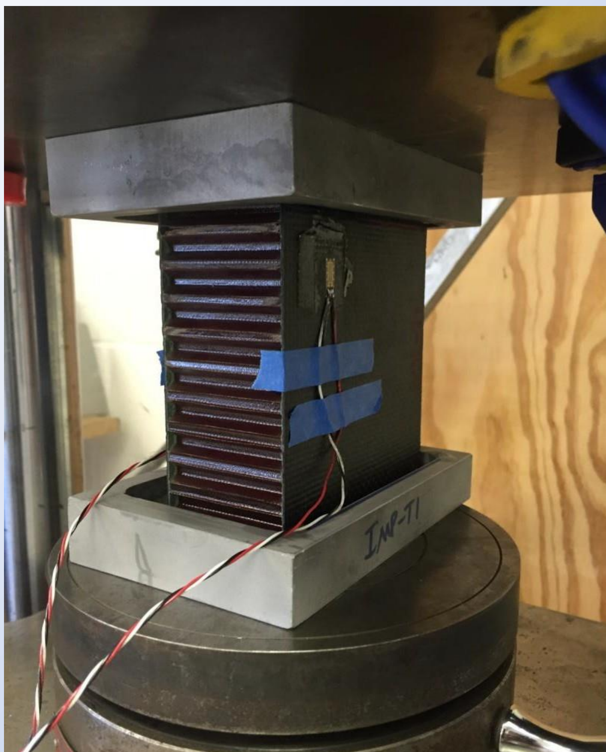

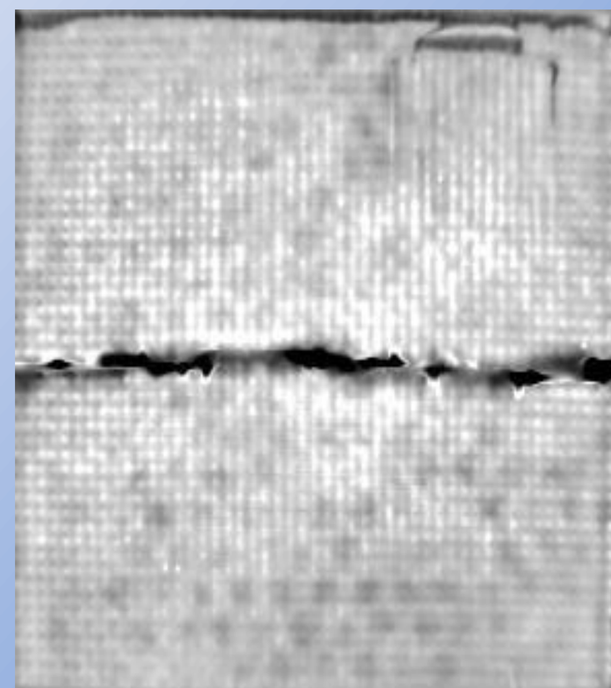

Drop-Weight Impact/CAI Test Results

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Test Group	Absorbed Energy (J)	Max Contact Force (N)	Contact Duration (ms)	Velocity Slowdown (%)	Damage Zone Dimensions		CAI Strength (ksi)
					Width (mm)	Length (mm)	
Virgin (without CNTs)	2.10±0.07	1044±68.9	5.35±0.06	53.7±3.74	0.93±0.04	0.98±0.13	343±9.86
Treated (with CNTs)	2.07±0.08 (-0.92%)	1101±49.8 (+5.53%)	5.19±0.11 (-2.94%)	56.8±2.57 (+5.88%)	0.85±0.04 (-9.52%)	0.93±0.09 (-4.55%)	375±19.2 (+9.27%)

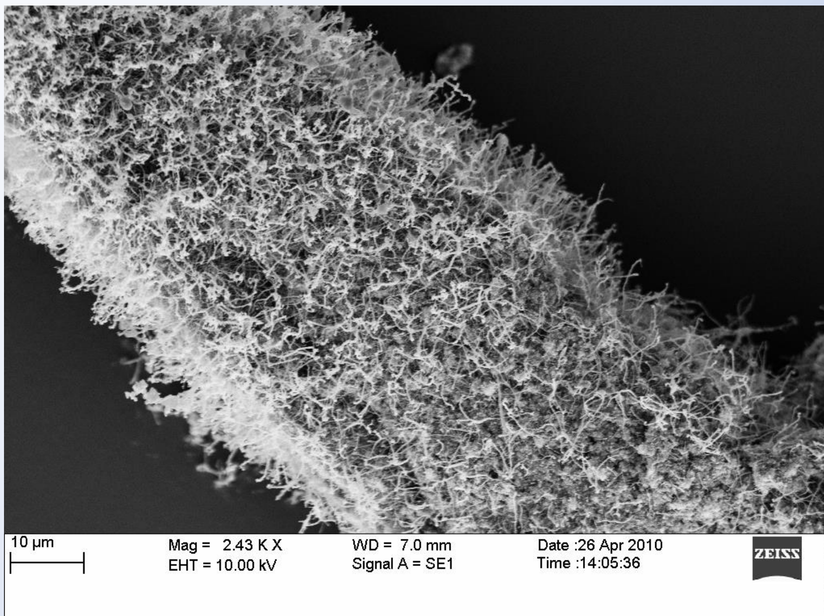
- PopTube Technology CNT synthesis process leads to:
  - Approximately 14% reduction in damage zone size
  - Approximately 9% improvement in CAI
- PopTube Technology provides for:
  - Improved resistance to damage from a given impact event
  - Improved damage tolerance (less strength knockdown) to a given impact event

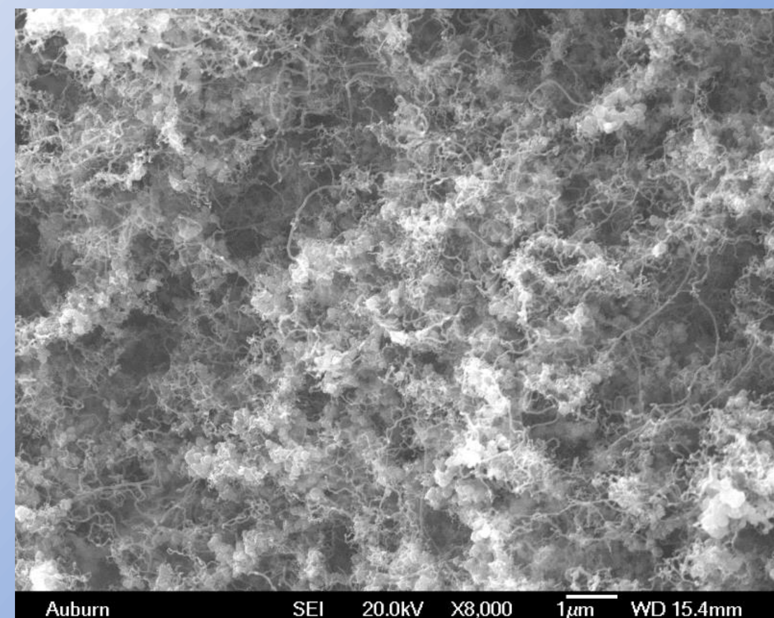
Growing CNTs with Non-Iron Metallocenes

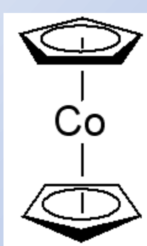
- Background
- The innovation
- Mechanical Properties Characterization
- **Growing CNTs with non-iron metallocenes**
- Bond Strength between CNTs and the Fibers
- Conclusion and future research

Non-Iron Metallocenes

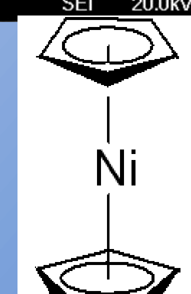
To evaluate weather less damage can be induced to carbon fibers by using metallocene with transition metals other than Fe as a precursor because Fe can react with carbon.







Bis(cyclopentadienyl) cobalt (II)



Bis(cyclopentadienyl) nickel (II)

Fiber tensile strength

Single fiber tensile strengths of PopTube Technology-treated fibers via various metallocenes.			
Test Group	Mean Tensile Strength (MPa)	Relative Change (%)	Estimated Characteristic Flaw Size (µm)
Virgin	3525 ± 475	-	-
PopTube Technology (Fe)	3033 ± 310	-14.0%	1.59
PopTube Technology (Co)	2932 ± 494	-16.8%	1.71
PopTube Technology (Ni)	2704 ± 1187	-23.3%	2.01

- Ferrocene induces the least amount of damage in the fibers.
- Nickelocene is shown to be the most damaging to the fibers.
- Coupled with the fact that ferrocene is known to provide for the best coverage and growth of CNTs, it is the ideal metallocene to use in the PopTube Technology CNT synthesis process.

Bond Strength between CNTs and the Fiber

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- Background
- The innovation
- Mechanical Properties Characterization
- Growing CNTs with non-iron metallocene
- Bond Strength between CNTs and the Fiber
- Conclusion and future research

Experimental Set-up

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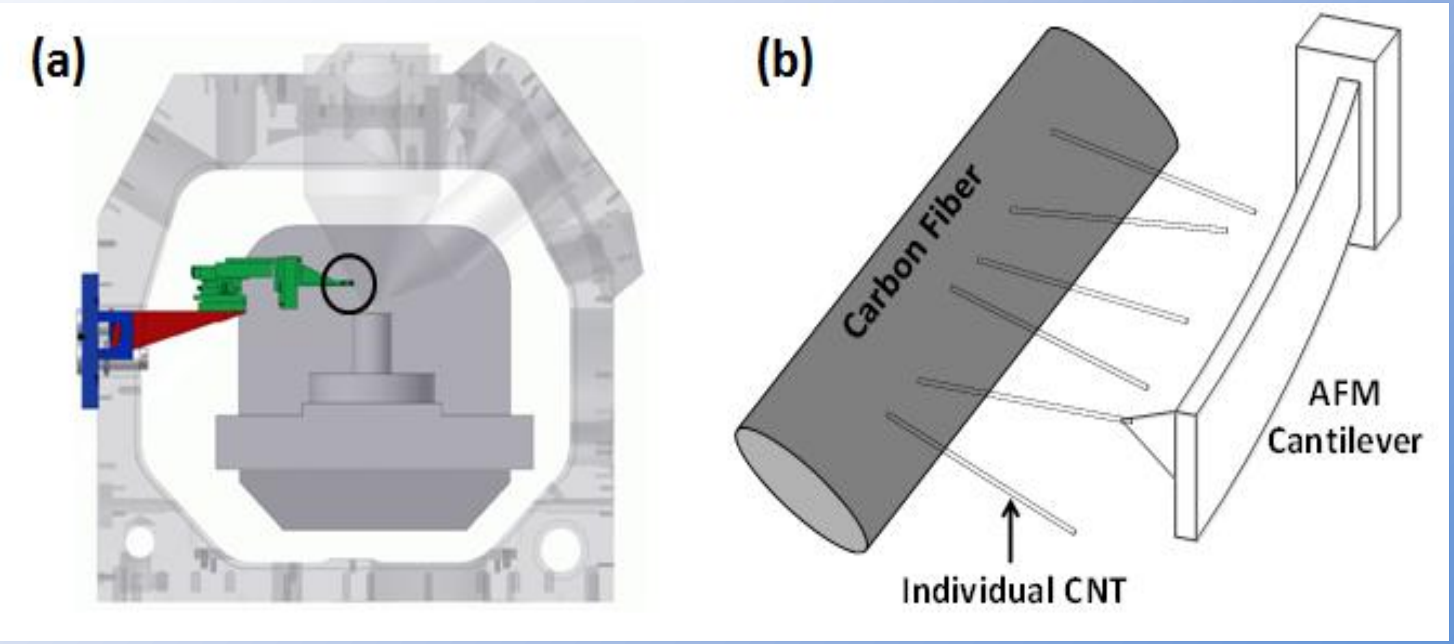
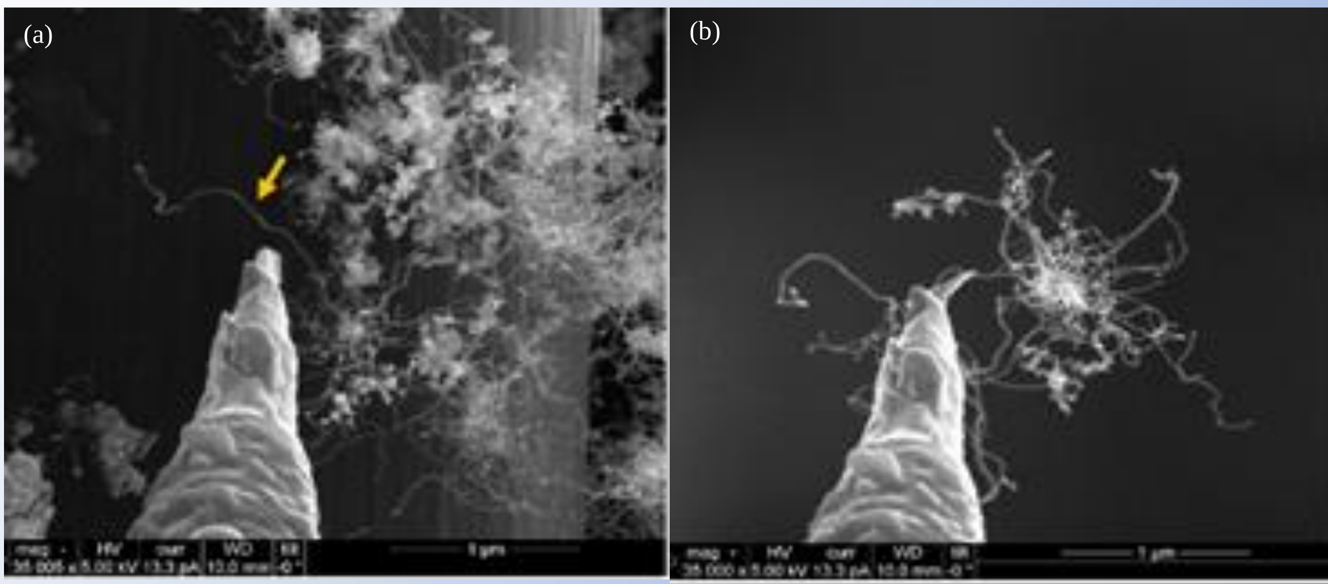
- The objective of this test to evaluate the bond strength between the CNTs and carbon fibers, which is critical to the effectiveness of the CNT reinforcement.
- A nanomechanical testing setup at NCSU was used.



Negligible Adhesion Force



- Very low adhesion between CNTs and carbon fibers.
- When the sharp tip was moved close to the CNT, the CNT and a neighboring CNT aggregate suddenly jumped onto the W tip and could not be taken away owing to strong electrostatic force.

Low Tensile Strength of CNFs

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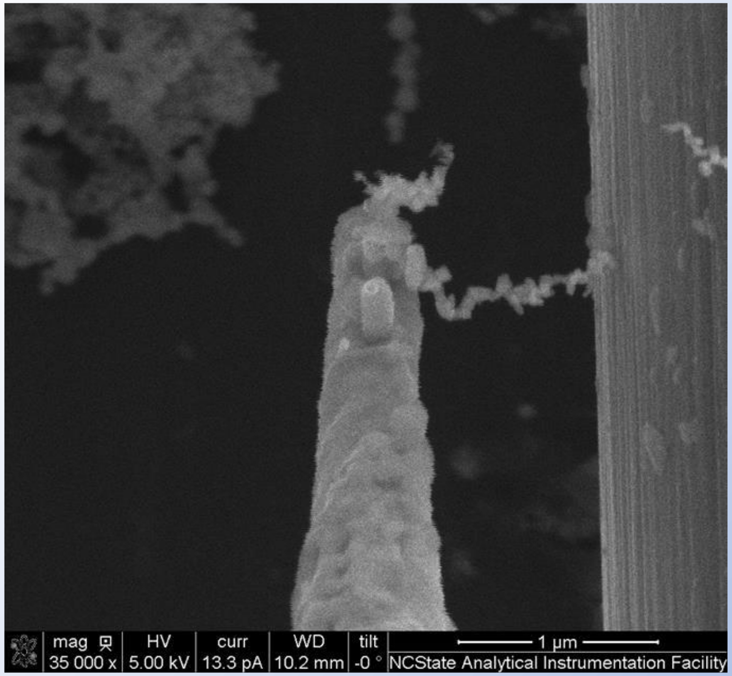

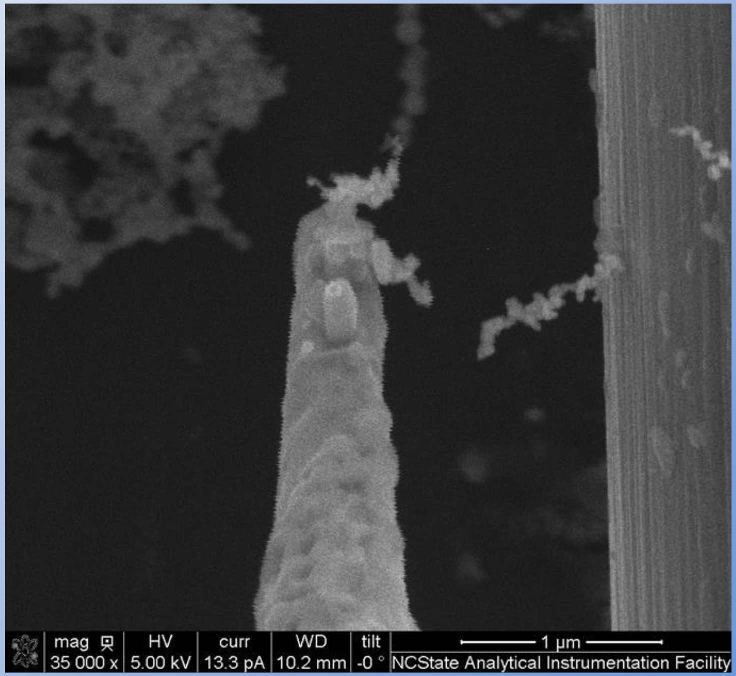

- In this case, the produced CNF was broken before it was pulled off the fiber.

Conclusions

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- Poptube Technology has ben successfully used to in-situ grow CNTs on carbon fabrics. However, it is rather difficult to control the quality of the produced CNTs.

- A comprehensive experimental program suggesting that Poptube Technology can
  - Significantly improve mode I initiating fracture toughness and interlaminar shear strength of composites.
  - Slightly improve mode II fracture toughness and low-speed impact resistance.
  - Introduce damage to the fibers, and therefore, reduce the uniaxial tensile strength of the composites. However, this reduction in the tensile strength can be mitigated through applying sizing to the fabrics grown with CNTs.

- Growing CNTs on carbon fibers using Ni and Co based metallocene does not reduce the damage to the fibers.

- Adhesion between the CNTs and carbon fiber is negligible.